

# Thermal Shifts in the Energy Levels of $\text{LaF}_3:\text{Nd}^{3+}$ \*

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We have measured the temperature dependence of the linewidths and positions for a number of transitions in the spectrum of  $\text{LaF}_3:\text{Nd}^{3+}$ . As the temperature increases, all lines broaden because of relaxation and Raman scattering of phonons. Relative to the ground state, all observed levels shift to lower energies as the temperature increases. Most lines show the usual shifts to the red. All these effects are qualitatively attributable to lattice vibrations. In general, the level shifts increase for the higher levels so that, ordinarily, line shifts are to the red with increasing temperatures. However, because of irregularities of the magnitudes of the level shifts, a few lines show shifts to the blue with increasing temperature, over some temperature ranges.

INDEX HEADINGS: Crystal spectra; Lanthanum fluoride; Neodymium; Absorption spectra; Emission spectra.

RECENTLY there has been considerable interest in the factors determining the widths and positions of sharp spectral lines from ions in crystals. In part, this has been motivated by the use of such lines in optical masers, where the linewidth controls the available gain. The wavenumber of the line plays an important part in determining the laser-output frequency. The sharper the spectral line, the more precisely it localizes the laser-output frequency.<sup>1</sup> Moreover, the temperature dependences of the linewidth and position display different, but related, interactions between the ions and crystal-lattice vibrations.<sup>2,3</sup> Thus, we are also led to study line widths and thermal shifts, in order to learn about the nature of these interactions.

As the host temperature is increased, the optical spectral lines are usually observed to broaden and shift to the red. Paetzold<sup>4</sup> has shown that the shifts are not primarily due to thermal expansion. Expansion of the lattice would shift the lines to the violet, opposite to the shift induced by applied pressure. Since the observed shifts are usually to the red as temperature increases, the line shifts cannot be attributed to the changes of the average distance between atoms. Indeed, for simple spectra with one or two lines well separated from any others, the thermal shift to the red is found to be proportional to the square of the amplitude of the lattice vibrations, i.e., to the total heat.<sup>5</sup>

However, Paetzold noted that some of the visible absorption lines of  $\text{Nd}^{3+}$  in the hydrated salt  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  showed shifts to the violet over portions of the

temperature range. These shifts are attributed to the direct effects of thermal expansion outweighing the effects of vibration. Expansion and its effects might be expected to be unusually large in a relatively soft, hydrated crystal of this sort. We have, therefore, been led to study the thermal shifts of the corresponding Nd lines in a harder ionic crystal,  $\text{LaF}_3$ .

The trivalent neodymium ion has a fairly complicated spectrum, especially in a crystal which provides sites of such low symmetry ( $C_{2v}$ ) as does  $\text{LaF}_3$ .<sup>6</sup> However, the  $\text{LaF}_3:\text{Nd}^{3+}$  is a laser system,<sup>7</sup> and we have, therefore, studied not only the line group corresponding to that observed by Paetzold, but also some other lines, including those for which laser action has been observed.

## I. EXPERIMENTAL PROCEDURE

Unoriented crystals of  $\text{LaF}_3$ , doped with trivalent neodymium, were obtained from Varian Associates, Palo Alto. The doping ranged from 0.1% to 4%; the majority of the work was done with crystals of 1%  $\text{Nd}^{3+}$  concentration.

Absorption and emission spectra were identified photographically with a 1.5-m Bausch & Lomb dual grating spectrograph. The gratings yielded dispersions of 8.1 Å/mm and 4.0 Å/mm, respectively. Kodak IN and 103-0 plates were used. In order to increase the speed of the spectrograph, a quartz cylindrical lens (length 250 mm, width 25 mm) of 75-mm focal length was placed near the plate holder in the path of the diffracted light. This arrangement served to reduce the length of photographic images of the entrance slit by a factor of 15/2, with a proportionate increase of speed. Positions and thermal shifts of the  $\text{Nd}^{3+}$  transitions were measured in relation to standard reference lines superimposed on the data plates. A Grant Instruments, Inc., line comparator, or graphic traces of the plate obtained from a Jarrell-Ash 23-100 recording microphotometer, were used to measure plate distances.

In a number of cases, linewidths and positions were measured with a high-resolution Jarrell-Ash 78-400,

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<sup>1</sup> L. F. Mollenauer, G. F. Imbusch, H. W. Moos, A. L. Schawlow, and A. D. May, in *Proceedings of the Symposium on Optical Masers* (Polytechnic Press, Brooklyn, New York, 1963), p. 51.

<sup>2</sup> D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).

<sup>3</sup> W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. 136 A271 (1964) and references therein.

<sup>4</sup> H. K. Paetzold, Z. Physik 139, 129 (1951).

<sup>5</sup> G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. 133, A1029 (1964).

<sup>6</sup> E. Y. Wong, O. M. Stafsudd, and D. R. Johnston, Phys. Rev. 131, 990 (1963); W. F. Krupke, Phys. Rev. 145, 325 (1966).

<sup>7</sup> L. F. Johnson, J. Appl. Phys. 34, 879 (1963).

1.8-m Ebert scanning spectrometer. RCA 7265 (S-20) or RCA 1702 (S-1) photomultipliers were used to detect the signal.

Sample temperatures were controlled by direct immersion in liquid coolants. Intermediate temperatures were attained with a gas blower. Temperatures ranged from 4.2° to 300°K and were measured, using thermocouples inserted in the crystal.

## II. RESULTS AND INTERPRETATION

A number of recent papers have reported the energy-level scheme of  $\text{LaF}_3:\text{Nd}^{3+}$ .<sup>6,8</sup> The impurity-ion site may be considered to have  $C_{2v}$  symmetry. In this coordination, all degeneracy, except the Kramers degeneracy, is lifted in the weak-field  $J$ -states. Transitions occur via electric-dipole perturbations. The relevant energy-level scheme of  $\text{Nd}^{3+}$  in  $\text{LaF}_3$  is shown

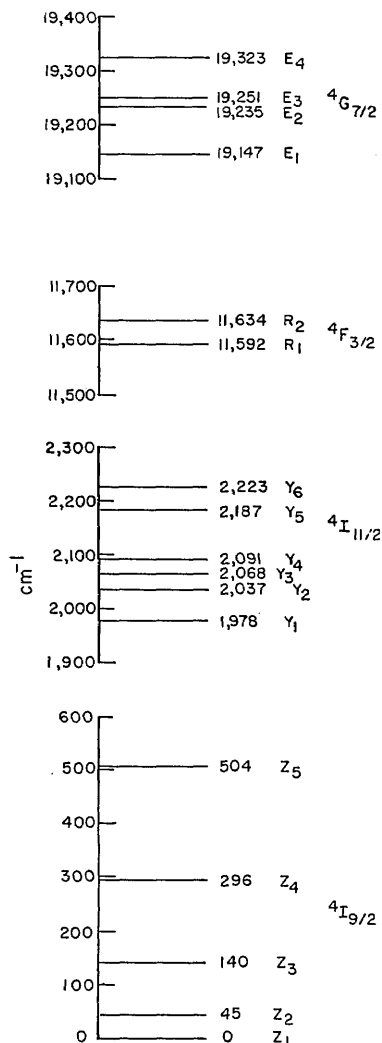


FIG. 1. Schematic representation of relevant energy levels in  $\text{LaF}_3:\text{Nd}^{3+}$  at 4.2°K.

<sup>8</sup> H. H. Caspers, H. E. Rast, and R. A. Buchanan, J. Chem. Phys. 42, 3214 (1965).

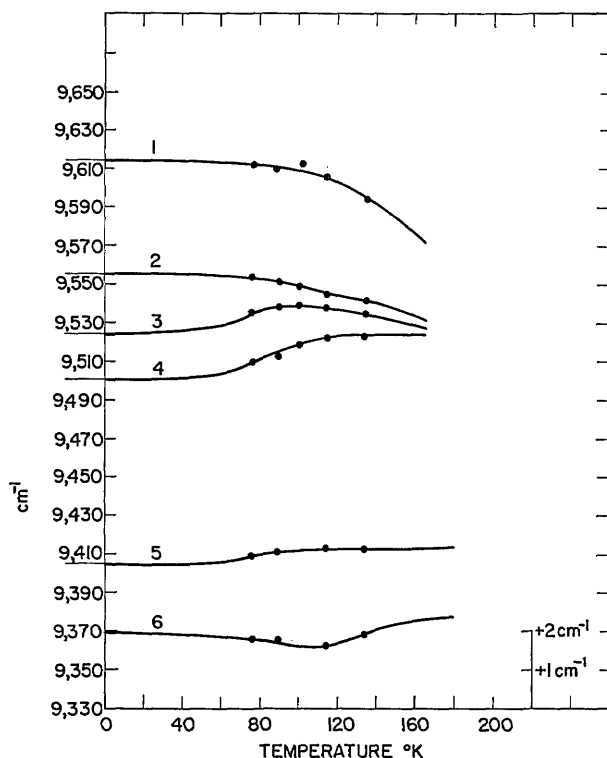


FIG. 2. Thermal shifts of some of the  $R \rightarrow Y$  fluorescence transitions of 1% $\text{Nd}^{3+}$  in  $\text{LaF}_3$ . Displacements are plotted on a 20-times expanded scale.

in Fig. 1. Level designation and nomenclature is that normally encountered in the literature.<sup>9</sup>

We restrict our presentation to three sets of transitions of particular interest. The so-called  $R$ -states ( $^4F_3$ ) of  $\text{Nd}^{3+}$  give rise to the familiar strong fluorescence in the near ir. The line positions of two sets of transitions involving this state, i.e., the  $R_1(^4F_3) \rightarrow Y_i(^4I_{9/2})$  fluorescence and the  $Z_i(^4I_{9/2}) \rightarrow R_1(^4F_3)$  absorption, have been investigated as functions of temperature. Results are shown in Fig. 2 and Fig. 3. The low-temperature reference positions from which the shifts were measured are also summarized in Fig. 1. Fixing the energy reference point as the ground state, i.e., assuming that  $Z_1(^4I_{9/2})$  is stationary, we give the net thermal shift of the  $R_1$  level in Fig. 3. This shift of the term value must be subtracted from those in Fig. 2 in order to obtain the shift of the term values of the  $Y$ -manifold. Such adjustment is indicated in Fig. 4. Thus, even though the peak positions of the  $R \rightarrow Y$  transitions manifest shifts to the red, as well as to the violet, as the host temperature is increased (Fig. 2), the net shift of each of the  $R$  and  $Y$  levels appears to be uniformly to the red.

The results of the measurements of the thermal line shifts of the  $E(^4G_{7/2}) \rightarrow Z(^4I_{9/2})$  transition are shown in Fig. 5. Again all lines, in contrast with Paetzold's

<sup>9</sup> E. H. Carlson and G. H. Dieke, J. Chem. Phys. 34, 1602 (1961).

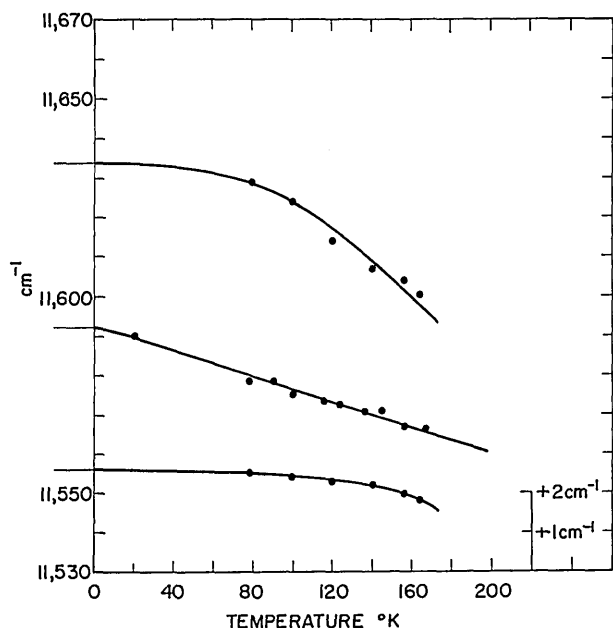


FIG. 3. Thermal shifts of some of the  $Z \rightarrow R$  absorption transitions of  $\text{LaF}_3:1\%\text{Nd}^{3+}$ . Displacement scale expanded by a factor of 20.

results, shift towards longer wavelengths as temperature is increased.

Many of the effects of crystal-lattice vibrations on ionic spectra can be described by quasistatic statistical models.<sup>2,3,5</sup> We begin our discussion with the experimental observation that stress-induced static deformations of the crystal displace the spectral lines by amounts depending on the magnitude and direction of the stress. Thus, at low temperatures, some spectral lines would have vanishingly small widths except for inhomogeneous broadening caused by random strains in the crystals.<sup>10</sup>

The line frequency of a spectral line in a crystal subjected to a static strain  $\epsilon$  may be written

$$\nu = \nu_0 + C_1\epsilon + C_2\epsilon^2 + \dots$$

Experimentally, the coefficient  $C_1$  can be measured for the various components of the stress tensor, but the attainable strains are too small for the effects of the quadratic term to be observable. However, the amplitude of the lattice vibrations is so large that the quadratic term has a substantial effect on the line positions. Even at the lowest temperatures, there is a shift of all the lines because of zero-point vibrations.<sup>11</sup> Ordinarily this is not observable, but it leads to an isotope shift if the impurity ion has several isotopic species. At higher temperatures, the increased amplitude of lattice vibrations, through this quadratic term, causes further shift in the same direction.

<sup>10</sup> A. L. Schawlow, in *Advances in Quantum Electronics*, J. R. Singer, Ed. (Columbia University Press, New York, 1962), p. 50.

<sup>11</sup> G. F. Imbusch, W. M. Yen, A. L. Schawlow, G. E. Devlin, and J. P. Remeika, *Phys. Rev.* **136**, A481 (1964).

Vibration-induced shifts may be expected to be predominately towards the red as the temperature increases. This follows because the dominant effect of the vibrations is to mix wavefunctions of the levels, which then repel each other. Since the density of the levels generally increases with the energy, there are always more levels above a given level to repel it downwards. Moreover, the upper level in any transition is closer to the repelling levels and so has smaller-energy denominators. It is, thus, shifted downward more than the lower level. If the spacing between levels lies in the range of lattice-vibration frequencies, those phonons resonant with the level spacing can be especially effective in coupling the energy levels.<sup>3</sup>

Shifts caused by thermal expansion, on the other hand, can be of either sign. As the crystal expands, the cubic and lower-symmetry crystal-field strengths decrease. All levels are shifted to a greater or lesser extent. The spacings between them, that is the transition frequency, may shift either way. However, thermal-expansion shifts are usually small.<sup>12</sup>

In addition to the shifts of the transition frequency, the phonon system is also responsible for the temperature-dependent broadening observed in the linewidths of transitions of ions in crystals. The dynamic lattice allows relaxation processes. These nonradiative processes are sufficiently rapid to limit the lifetime of the

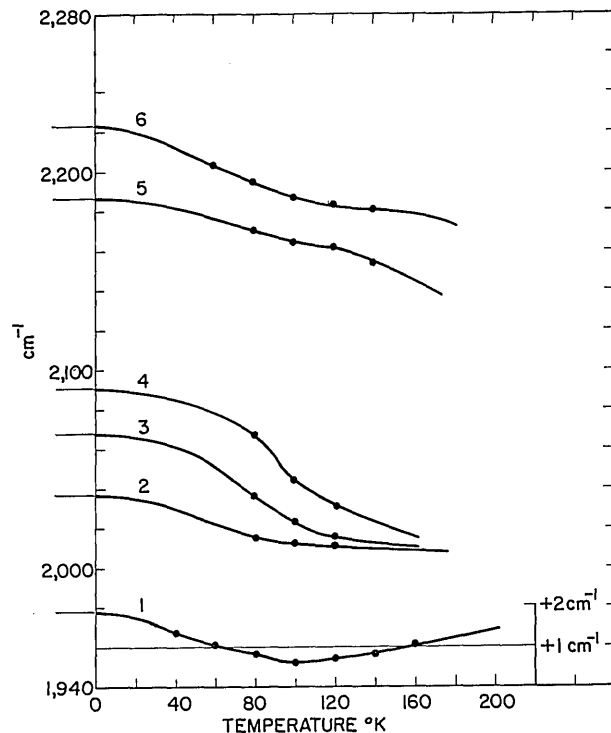


FIG. 4. Thermal shifts of the Y-manifold term values as extrapolated from Figs. 2 and 3. Displacement scale expanded  $\times 20$ .

<sup>12</sup> W. M. Yen, G. F. Imbusch, and D. L. Huber, in *Proceedings of Conference on Optical Properties of Ions in Solids* (John Wiley & Sons, Inc., New York, 1967).

relaxing state and thus to produce observable homogeneous broadening. The linear term in the stress expression may be shown to lead to single-phonon relaxation processes when there are nearby ( $E \lesssim k\theta_D$ ) electronic states to which the ion may relax. The quadratic term leads to Raman-type line broadening, which occurs even with isolated levels. The coefficients encountered in the rigorous expressions for the temperature dependence of the line shift and linewidth arise from the same basic mechanism and are thus interrelated. It follows, then, that if the Raman broadening coefficient is large, the corresponding quadratic term in the line shift will also be large and a red shift with increasing temperature will result.

For the case in point, the strain-uncorrected widths of some of the  $R \rightarrow Y$  fluorescence lines of  $\text{Nd}^{3+}$  are shown in Fig. 6 as functions of temperature. We may use plots of this type to estimate the relative importance of linear and quadratic terms. The zero-temperature intercepts of the widths are measures of the strengths of the single-phonon processes; from Fig. 6, the value of this coefficient is of the order of  $0.5 \text{ cm}^{-1}$ . On the other hand, the rapid increase of the linewidth with temperature indicated in the figure is characteristic of a predominant Raman process. Thus, it is not surprising that the shifts of the term values of these interacting manifolds all show net shifts to the red as temperature increases (Figs. 4 and 5). The effect of the single phonon term is to introduce a slight repulsion of the  $J$  Stark levels, thus, the lower-energy terms are further shifted downward, whereas the higher-energy levels are

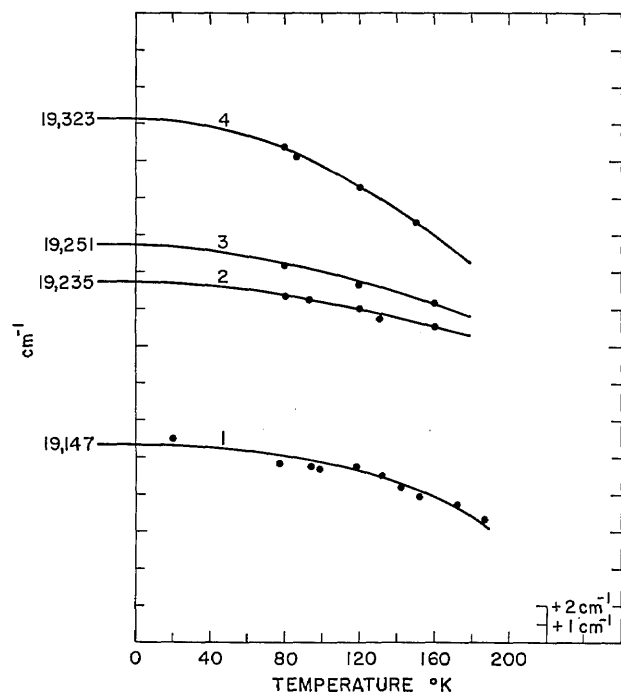


FIG. 5. Thermal shifts of the  $Z \rightarrow E$  transition. These lines are to be contrasted with results in Ref. 4. Displacement scale expanded  $\times 10$ .

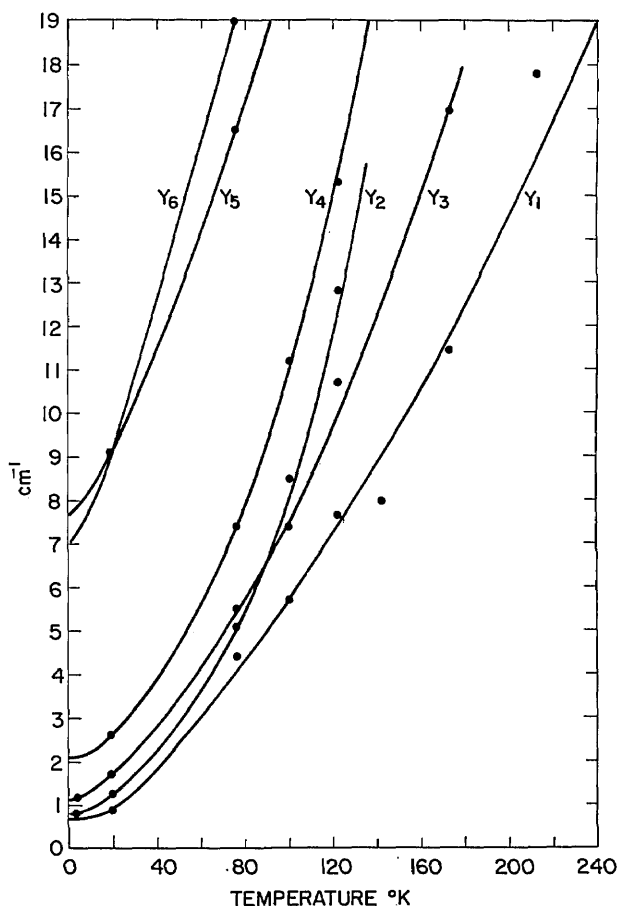


FIG. 6. Broadening of the  $R \rightarrow Y$  transitions as a function of temperature, indicating large quadratic contribution from the lattice vibrations.

shifted upward. That this is the case may be verified by inspection of Fig. 2. The transitions 5 and 6 appear to be anomalous; however, this analysis does not take into account the exact details of the system, and we have not attempted to determine all the parameters necessary to obtain a quantitative fit to the exact expressions.

For the  $E$  states, it follows from the direction of the temperature-dependent shift that again we are observing predominantly the quadratic term. Thus, we must conclude, following Paetzold's conjecture, that for harder ionic lattices, the energy levels of the  $\text{Nd}^{3+}$  ion are not substantially affected by thermal changes of the lattice parameters.

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